GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 12/10/80

Project Title: Feasibility Study for Alternative Fuels Production

Project No: A-2820 (Sub-project is E-19-631/Roberts/ChE)

Project Director: Mr. Paul H. Butler

Sponsor: Nuclear Assurance Corporation; 24 Executive Park West; Atlanta, GA 30329

~~5/15/81~~ 9/31/81 ~~6/30/81~~

Agreement Period: From 10/15/80 Until ~~4/30/81~~

Type Agreement: Contract dated November 5, 1980 (under DOE Grant No. DE-FG-180RA50322)

Amount: $70,278 A-2820
$15,703 E-19-631
$85,981 TOTAL

Reports Required: Subtask 1.1 Report; Interim Report; Subtask 1.8 Report; Final Report

Sponsor Contact Person (s):

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 6/8/82

Project Title: Feasibility Study for Alternative Fuels Production

Project No: A-2820

Project Director: Paul H. Butler

Sponsor: Nuclear Assurance Corporation

Effective Termination Date: 7/31/81

Clearance of Accounting Charges: _____

Grant/Contract Closeout Actions Remaining:

NONE; Complete

- ☐ Final Invoice and Closing Documents
- ☐ Final Fiscal Report
- ☐ Final Report of Inventions
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FORM OCA 10:781

Please replace the last letter with this revised Quarterly report

Georgia Institute of Technology
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

February 5, 1981

Nuclear Assurance Corporation
24 Executive Park
Atlanta, Georgia 30329

Attention: Mr. L. T. Gregg

Subject: Feasibility Study for Alternative Fuels Production
Quarterly Progress Report, A-2820

Dear Sir:

In accordance with your request at our last Project Review Meeting, we are transmitting a copy of our Quarterly Progress Report on the 1000 ton per day Wood-to-Ethanol Feasibility Study.

If you have any questions please contact me.

Sincerely,

Paul H. Butler
Project Director

jw

Attachment

cc: H. O. Spauschus
N. McHan ✓

FEASIBILITY STUDY FOR ALTERNATIVE FUELS PRODUCTION
DOE GRANT NO. DE-FG-180RA50322 (Project A-2820)

Quarterly Progress Report
October 15, 1980 through January 31, 1981

I. Summary of Accomplishments

The contract coverage on the project was received and work began on October 15, 1980. The first Kickoff meeting including all subcontract elements of the project team was held on October 16 1980 at Georgia Tech. At this meeting it was disclosed that Georgia Tech had received a 1 ton reactor from Stake Technology, Ltd. for evaluation as the pretreatment and hydrolytic portion of the GIT process. Subsequent testing activities have determined that the unit is ideally suited for this purpose provided certain minimum changes in its design can be made in the larger sized equipment, such as, materials of construction and control of biomass residence times.

In accordance with our contract a Conceptual Flow Diagram and a listing of the design operating conditions were delivered to N.A.C. on November 17, 1980. On December 16, 1980 a Preliminary Technology Assessment Report was delivered which presented an evaluation of alternative or competitive processes for the conversion of lignocellulose to ethanol.

During the months of December and early January considerable testing was undertaken utilizing the STAKE Reactor. The data indicated that a change in the process would be desirable and

a revision from using ethanol for lignin extraction to the use of sodium hydroxide was made. This revision reduces the capital equipment cost by eliminating the need for expensive solvent recovery systems. As a result of this major testing effort, sufficient kinetic data was developed in order that a realistic material balance could be produced. This was presented in the Project Review meeting on January 23, 1981 and revised and submitted on January 28, 1981.

It was recognized that the material balances as issued were for hardwood chips and shows a slightly greater reduction in the yields than was anticipated. Previous literature search and limited bench scale testing indicated a projected yield of 69.3 gallons of anhydrous ethanol per oven-dry ton for softwoods and 59.6 gallons per ODT for hardwoods. The material balances which were developed during this study project about 56.8 gallon of anhydrous ethanol per oven-dry-ton of hardwood. The research team is pursuing certain improvements to the present process which should bring our projected yield back to more desirable levels.

ETHANOL YIELDS
(Gallons per ODT)

	HARDWOOD		SOFTWOOD	
	95%	ANHYDROUS	95%	ANHYDROUS
Previous Projection for Batch System	62.7	59.6	72.9	69.3
Current Projection for Continuous System	59.8	56.8	-NOT PERFORMED-	

The Final Technology Assessment Report is in process of revision and updating and will be submitted during the month of February.

II. Significant Problem Areas:

None

III. Schedule Projection

At the present no problems exist which will adversely affect the planned completion of the study.

A-2820

Georgia Institute of Technology
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

February 16, 1981

Nuclear Assurance Corporation
24 Executive Park
Atlanta, Georgia 30329

Attention: Mr. L. T. Gregg

Subject: Feasibility Study for Alternative Fuels Production; Final Technology Assessment Report, A-2820

Dear Sir:

In accordance with the terms of the subject contract scope of work, we are transmitting five copies of the Technology Assessment Final Report.

Also transmitted is one original of the revised Flow Diagram for the proposed 1000 ODT/D Wood-to-Ethanol Plant.

If you have any questions, please contact me.

Sincerely,

Paul H. Butler
Project Director

Encs. Technology Assessment-Final Report (5 copies)
Flow Diagram-Original (1 copy)

cc H. O. Spauschus
N. McHan, OCA

"FEASIBILITY STUDY FOR ALTERNATE FUEL PRODUCTION"
STATE OF THE ART TECHNOLOGY ASSESSMENT
OF ACID HYDROLYSIS OF BIOMASS
(Final Report)

*M. K. Bery
*P. H. Butler
*A. R. Colcord
**R. S. Roberts

*Engineering Experiment Station

and

**School of Chemical Engineering
Georgia Institute of Technology

Prepared For:

Nuclear Assurance Corporation
24 Executive Park West
Atlanta, Ga. 30329

February 1981

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I. STUDY PERSPECTIVE

The amount of petroleum used for transportation in the U.S.A. is about 8,000,000 barrels daily. Based on current growth rates, by 1990 the U. S. will be consuming 9,000,000 barrels of petroleum daily. This clearly indicates that a very large market for an alternate liquid fuel is developing. Thus projected shortages in liquid fuel supply, tax credit incentives offered by the U. S. government and availability of research funds from the DOE has led to a substantial research and development activity for the conversion of biomass into ethanol.

Technology to produce ethanol from grains, fruits and molasses has existed for centuries. The earliest studies of ethanol production by the hydrolysis of cellulosic biomass were carried out in Germany. Two commercial scale processes were developed; a dilute acid hydrolysis method attributed to Scholler and a concentrated acid method by Rheinau. These two processes were the basis for more advanced processes being developed at present.

Mitre Corporation[1] has evaluated technological and economic factors of the production and use of biomass based alcohol fuels relative to achieving five or ten percent alcohol-gasoline blends by 1990. Mitre[2] has also reviewed fourteen studies and reports in which the economic aspects of producing ethanol from various biomass feedstocks have been evaluated. These studies presented 28 ethanol plant configurations. The major assumptions made and the financial and cost performance criteria used for each parameter are identified.

Georgia Tech, under contract with the Department of Energy, has thoroughly evaluated technologies used to convert biomass

into ethanol. Conversion of cellulosics to ethanol involves four major steps:

- Pretreatment of raw material
- Hydrolysis of pretreated cellulosic feedstock into fermentable sugars
- Fermentation of sugars to produce ethanol
- Recovery of ethanol.

Most of the advances in conversion technology have been made in the pretreatment and hydrolysis steps. These topics are discussed in Sections II and III of this report. Section IV describes new processes still in the development stage while Section V contains the conclusions drawn from this study.

II. PRETREATMENT PROCESSES

To utilize the cellulose contained in biomass effectively some low cost method of changing the nature of the cellulose and disrupting its physical association with lignin must be developed. A number of chemical, mechanical and thermal pretreatment methods have been evaluated. The chemical pretreatment methods are not universally applicable with the exception of delignification.

Mechanical pretreatment involving ball milling[3,4] is a very good approach to making the cellulose available for hydrolysis, however, the power cost alone makes it too expensive. The use of two roll mill pretreatment shows a good deal of potential and power costs are within the range of feasibility, as shown in Exhibit II-1.

EXHIBIT II-1

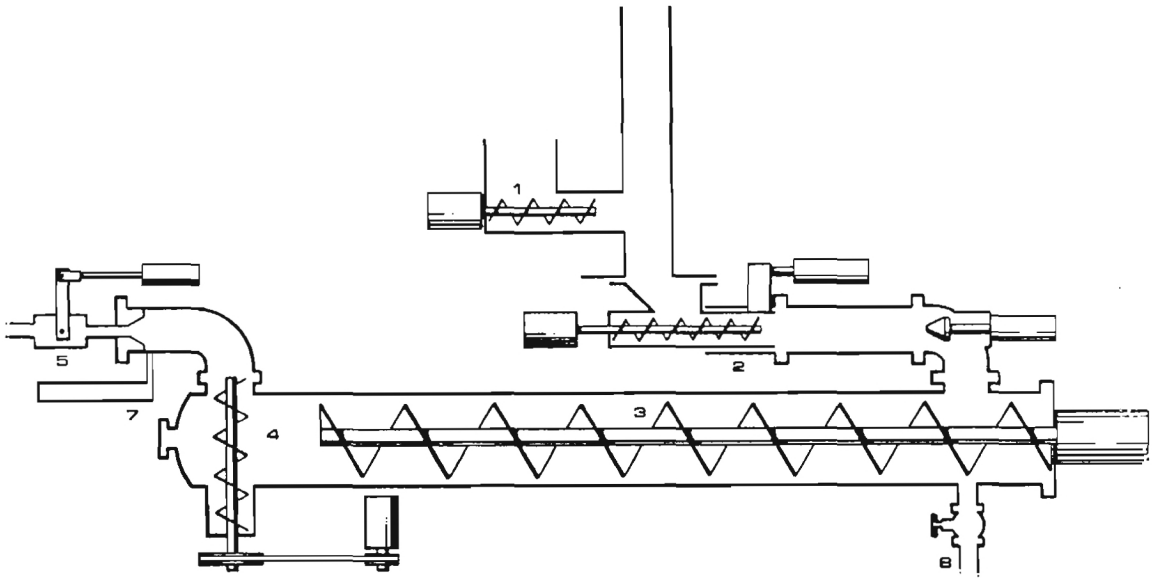
PRETREATMENT COSTS

Treatment	Power	Cost*
Ball Milling	1.4 kw-hr[4]	4.9¢
2 Roll Milling	.25 kw-hr[8]	0.9¢
	.66 kw-hr[9]	2.3¢
Steam Explosion	0.7-1.3 lbs steam[10]	0.28- 0.52¢

*Basis: 1 pound of wood
electric power cost @ $3.5/kw-hr
steam costs $4.00/1000 lb

The process which looks the most promising at this time, both from an operating cost and capital investment standpoint, is the steam explosion process. Iotech Corporation,[5] a Canadian firm, has developed a batch system for pretreatment. Biomass is fed to the system, steam pressure is raised to a predetermined pressure between 600 and 1000 psi, maintained at that pressure for 1 to 3 minutes, and then decompressed through a quick opening valve. During this operation some of the hemicellulose is hydrolyzed by autohydrolysis, thus making the lignin very easy to extract. Stake Technology,[6] another Canadian company, has developed a reactor illustrated in Exhibit II-2 which carries out steam explosion continuously at a relatively low pressure of 300 to 600 psi. This lower pressure is a significant improvement in the pretreatment step which is presently being evaluated by a team of Georgia Tech research personnel.

Tsao[7] at Purdue has developed a unique process which takes a completely different approach than those previously described. The basis for Tsao's process is that if cellulose is dissolved and then precipitated the cellulose structure is separated from the lignin and changed from the crystalline form to more reactive amorphorous structure. Amorphorous cellulose is readily hydrolyzed to fermentable sugars by both acids and enzymes. To produce amorphorous cellulose from biomass Tsao proposes the following process. The biomass is first prehydrolyzed with dilute sulfuric acid to remove the hemicellulose. The remaining residue is washed and dried to a suitable moisture content and then dissolved in concentrated sulfuric acid. Other solvents have been proposed but the present choice is 70 percent sulfuric acid. After dissolution the cellulose is rapidly precipitated by the addition of methanol. The precipitated cellulose along with the lignin is subsequently subjected to enzymatic or acid hydrolysis.



ANIMAL FEED PRODUCTION SYSTEM

MAIN SYSTEM COMPONENTS

1 – METERING FEED SCREW
2 – PLUG FEEDER
3 – STEAM TUBE & PROPELLING SCREW
4 – DISCHARGE SCREW
5 – EXPANSION CONTROL VALVE
6 – DISCHARGE TO PRODUCT STORAGE
7 – NITROGEN ADDITION SYSTEM
8 – FROM STEAM GENERATOR

Recovery of the concentrated sulfuric acid for reuse is a problem in this process. A fraction of the methanol used can be degraded, thus making this pretreatment method very expensive and probably not feasible. A number of solvents have been evaluated by Tsao and other investigators with little success. These are summarized in Exhibit II-3. A number of organic solvents listed in Exhibit II-4 have also been evaluated under appropriate reaction conditions. Most of these use high pressure to achieve the degree of delignification necessary. Because of severe operating conditions and a need for solvent recovery, organic solvent delignification becomes both energy and capital intensive.

The methods that have been investigated for pretreating lignocellulosic raw materials are summarized in Exhibit II-5.

EXHIBIT II-3
CELLULOSE SOLVENTS

Metal Complex Solutions

Cuoxam or Cuam	$\{Cu(NH_3)_4\}(OH)_2$
Cupriethylenediamine, Cuene, or CED	$\{Cu(en)_2\}(OH)_2$
Cu:Biuret:Alkali	
Cooxene	$\{Co(en)_3\}(OH)_2$
Nioxam	$\{NI(NH_3)_6\}(OH)_2$

Neutral Salts in Concentrated Aqueous Solution

$ZnCL_2$
$Ca(SCN)_2$
LiSCN, NaSCN, LiI, NaI, KI
$K_2(HgI_4)$

Strong Bases in Aqueous Solution

LiOH
NaOH
NaOH + ZnO
NaOH + BeO
Tetraethylammonium-hydroxide and some higher homologs
Trimethylbenzyl-ammoniumhydroxide (Triton B),
Dimethyldibenzyl-ammoniumhydroxide (Triton F)

Purdue-Tsao Solvents

"Cadoxen" (Ethylenediamine, Cadmium oxide, H_2)O
CMCS
Ethylene diamine
Sulfuric acid

Source: Reference 11.

EXHIBIT II-4
ORGANIC SOLVENT DELIGNIFICATION

Solvent System	Conditions of Extraction			% Delignification
	Temperature °C	Pressure psi	Duration hours	
Methyl Alcohol-H_2O	158	150	4	58.4
Ethanol-H_2O	165	150	4.5	67.4
n-Propanol-H_2O	172	150	4	76.4
Isopropanol-H_2O	162	150	4	62
n-Butanol-H_2O	174	150	4	87.2
Isobutyl Alcohol-H_2O	174	150	4	80.5
Tertiary Butyl Alcohol - H_2O	157	150	4	56
n-Amyl Alcohol-H_2O	177	150	4	82
IsoAmyl Alcohol-H_2O	177	150	4	84.1
Tertiary Amyl Alcohol - H_2O	159	150	4	60.7
Dioxane-H_2O	176	150	4	65.1
Acetone-NH_3	---	---	-	50
Cyclohexanone-NH_3	210	890	1.25	81.4
Methyl Ethyl Ketone- NH_3	210	860	2	76.08
Xylene Sulfonic Acid	100	150	1	80

Source: Reference 12.

EXHIBIT II-5
PRETREATMENTS

I. Chemical

Swelling with Alkaline Agents

(1) Sodium Hydroxide
(2) Ammonia

Delignification

(1) Pulping
(2) ClO_2
(3) Ammonium Bisulfate
(4) SO_2
(5) Sodium Chlorite
(6) Organic Solvents

Cellulose Dissolution

(1) Tsao/Purdue Process
(2) Cellulose "Solvents"

II. Physical

(1) Steam
    (A) Iotech
    (B) Stake Technology
    (C) GE
    (D) Autoclaving
(2) Grinding
    (A) Ball Milling
    (B) Roll Milling
(3) Irradiation
    (A) Gamma
    (B) UV
    (C) Heat
(4) Freezing
(5) Pressure

Source: Reference 13.

III. HYDROLYSIS PROCESSES

During this study, several hydrolysis processes were reviewed[13] and are summarized in this section. After a careful evaluation of enzymatic methods to produce fermentable sugars from cellulose it was concluded that at the present time it is not a commercially viable route to produce sugars. Main disadvantages are the high cost of enzyme production and unavailability of an efficient enzyme system. It was therefore concluded that only acid hydrolysis methods would be presented in this report.

Acid hydrolysis of wood is actually a simple chemical reaction. Either sulfuric acid or hydrochloric acid can be used as the catalyst for hydrolysis of wood. The wood hydrolysis can easily be carried out quantitatively in the laboratory, but the economic industrialization on a commercial scale has proven to be a difficult problem. The primary restraints have been the recovery of acid, finding of suitable acid resistant materials, designing equipment, and discovery of a simple way to refine sugar.

Concentrated sulfuric acid hydrolyzes wood quantitatively with little sugar degradation when sufficiently large quantities of acid are used. With concentrated hydrochloric acid the reaction reaches an equilibrium after a certain amount of time but the acid hydrolyzate is capable of continuing the hydrolysis if it contacts fresh wood. This fact has led to the development of a counter current system which produces solutions of up to 25 percent sugar.

The dilute sulfuric acid process was devised to overcome the difficulty of acid recovery. The processes using dilute acid

have to be carried out at elevated temperatures which results in the reduction of yields due to sugar degradation.

1. CONCENTRATED ACID HYDROLYSIS

(1) Hokkaido Process

The process known as the Hokkaido[14] was developed in Japan in 1948 to hydrolyze wood with concentrated sulfuric acid. In this process wood chips are first prehydrolyzed under conditions that depend upon whether furfural or xylose is the desired product from the reaction. If xylose is desired then, the prehydrolysis consists of reacting the wood with 1.2 to 1.5 percent sulfuric acid at 140° to 150° C. Furfural is produced when the pentose formed from the pentosans is directly converted by dehydration by steam at 180° to 185° C. The prehydrolyzed wood is dried and crushed, then the main hydrolysis is carried out by treating this crushed wood with 80 percent sulfuric acid at room temperature. The important prerequisite in the concentrated sulfuric acid process is the maintenance of a low mixing ratio of acid to wood without sacrificing sugar yield. To obtain the desired low mixing ratio a new mixing process was developed. In this process the dried powdered prehydrolyzed wood is mixed with acid of the correct concentration by spraying them together in a thin film. The mixing requires only about 30 seconds and the product is immediately filtered under pressure and washed. The sugar yield is greater than 90 percent with a mix ratio of 0.9 and about 96 percent with mix ratio of 1.0. The concentration of the sulfuric acid from the combined filtrate and washing water is 30 to 40 percent. This acidified sugar solution is treated with a diffusion dialysis using an ion exchange resin membrane to recover 80 percent of the total sulfuric acid as a 25 to 35 percent solution. The acid is concentrated by evaporation to 80 percent and reused. The sugar solution contains 5 to 10 percent gluclose polymer

and 5 to 15 percent sulfuric acid. During this dialysis 1.8 to 2 percent of the total sugars are lost. The sugar solution after dialysis is post hydrolyzed by heating at 100° C for about 100 minutes. The hydrolyzate is neutralized and the resultant calcium sulfate removed by filtration. The pH of the neutralized sugar solution is adjusted to 2.5 to remove the calcium ions and then the solution is concentrated to 50 percent. The sugar is separated as a double salt by adding the theoretical quantity of sodium chloride. After washing with cold water the gluclose is isolated in crystalline form. An overall yield of 286 to 296 kg/ton of wood is obtained which is 83 to 85 percent of the theoretical maximum.

J. Kobayashi[16] has proposed a modification of the Hokkaido process called the Thorough Drying Process. The primary advantage is that the large amount of power required to mix sulfuric acid and dry wood for the main hydrolysis is reduced. In this process wet prehydrolyzed wood is immersed in dilute sulfuric acid and after the acid is drained the wood is dried at 40 to 50° C by blowing with dry air. The sulfuric acid in the wood becomes concentrated as the drying progresses and the main hydrolysis is completed. Simultaneously, unit power consumption should be reduced and construction costs lowered with almost the same yields achieved through the Hokkaido process.

Another concentrated sulfuric acid process was developed by Nippon Mokuzai Kogaku Co.[14]. The main feature of this process is that the sulfuric acid is not recovered but converted into gypsum which is marketed as a by-product. The other products from this process are crystalline glucose, crystalline xylose and refined molasses. The major problem with all of these concentrated sulfuric acid hydrolysis processes is the difficulty of recovering the acid for reuse. In the absence of any such commercially viable acid recovery method the concentrated acid hydrolysis approach is considered to be infeasible.

(2) Berguis-Rheinau Process

Several processes have been developed which use concentrated hydrochloric acid to hydrolyze wood. The first commercial process is known as the Berguis-Rheinau[15] process. In this process the wood is hydrolyzed by immersing it in a 40 percent hydrochloric acid solution. The first cycle produces a 10 percent sugar solution. This acid solution containing sugar is reused several times for hydrolysis to obtain a sugar solution of about 40 percent. The 40 percent sugar solution is distilled under reduced pressure at 36° C to recover hydrogen chloride gas, thereby recovering about 80 percent of the hydrochlorid acid. The sugar solution is spray dried with hot air to expel residual hydrochloric acid. Lignin remaining in the reactor is washed with water to recover additional sugar and hydrochloric acid. The most difficult technical problem encountered in the early stage of development was the selection of suitable acid resistant materials for heaters and condensers. One difficulty lay in the transfer of heat for evaporation to recover the hydrochloric acid. Metal could not be used because of the corrosiveness of the acid and ceramic linings were unacceptable because of their low heat conductivity. To solve the problem a mineral oil which remained liquid at the required temperatures, which did not react with the HCL, and which did not emulsify with the hydrolyzate was used as a heat transfer medium. The hot oil in a fine spray was brought in contact with the acid hydrolyzate. Vapors which consisted of hydrochloric acid and steam were then removed and condensed to recover the acid. The remaining hydrolyzate was largely free of hydrochloric acid but was mixed with oil that was removed by decantation for reuse.

(3) Udic-Rheinau Process

The original Rheinau process has been improved in an attempt to make it economically feasible under peacetime conditions.

The improved process is known as the New Rheinau Process.[16] In this process crystalline glucose is the principal product. Two new processes of prehydrolysis and posthydrolysis are incorporated and chemical engineering studies have been made of hydrochloric acid recovery. In the improved process the wood was first immersed in 1 percent hydrochloric acid and then prehydrolyzed at 130° C under pressure to remove the hemicellulose. The prehydrolyzed wood which contains lignin and cellulose is dried and converted to glucose and dimer, trimer, and tetramer sugars with 41 percent hydrochloric acid in the main hydrolysis process. The lignin which remains after hydrolysis and extraction is washed with hydrochloric acid solution and then water. Hydrochloric acid is recovered by vacuum distillation of the acidified sugar solution. The resultant solution is 60 to 65 percent sugar of which one half is dimer and trimer sugars. The solution is diluted to 10 percent sugar concentration and posthydrolyzed. Since the primary product is crystalline glucose the sugar solution is deacidified and deionized with ion exchange resins, decolorized, refined and concentrated again to crystalline glucose. With the New Rheinau Process the hydrochloric acid losses are reduced from over 18 percent in the Bergius-Rheinau process to 5 or 6 percent. It has been found that no sugar is degraded if prehydrolysis is carried out at low temperatures with 35 percent hydrochloric acid. The New Rheinau Process is now called the Udic-Rheinau process. This method has a disadvantage associated with recovering concentrated hydrochloric acid by an energy intensive azeotropic distillation which adds to the overall cost of the process.

(4) Naguchi-Chisso Process

The hydrogen chloride gas process[17,18] is essentially a concentrated acid hydrolysis process. The reason for using hydrogen chloride gas is to shift the hydrolysis reaction into

the interior of the wood particles and to facilitate the recovery of the acid. In this process the wood is impregnated with a small quantity of highly concentrated hydrochloric acid and then the concentration is increased by passing hydrogen chloride gas into the wood. The acid can be recovered quickly simply by heating the wood.

Historically the Prodor process was the first pilot process developed using hydrogen chloride gas. In this process sawdust enters the mixer and is mixed with concentrated hydrochloric acid. A mixture consisting of 60 parts water, 46 parts hydrochloric acid and 100 parts dry sawdust is charged into the digester. The digester consists of 12 trays resembling a Herreshoft furnace. The mixture is swept alternately toward the center and the periphery of the trays by the rotation of blades where it falls to the next tray. Hydrogen chloride gas flows counter current to the flow of the sawdust acid mixture. After eight hours the hydrolyzed material comes off the bottom and is transferred to a drying section where the material is dried and the acid expelled by hot air. Because this process relies heavily on acid resistant structural materials which were not available the process was never successful.

A later process, the Darboven, used a tank filled with carbon tetrachloride as the reactor instead of the tray type used in the Prodor. Wood chips are suspended in carbon tetrachloride and hydrogen chloride gas is blown into the vessel. Hydrolysis take place as the concentration of the hydrochloric acid in the wood flour increases. The hydrolyzed material is dried by hot air after the carbon tetrachloride has been removed. The heat which is involved by the absorption of hydrogen chloride gas is removed by using the carbon tetrachloride as heat exchange medium. The equipment required for the Darboven process is simpler than that required for the Prodor process.

A still later process was developed called the Herneng process. Wood chips without any predrying are fed into the reaction column. The reaction column is a hexagonal column made of vinyl chloride having 40 inclined trays. The chips are mixed with 30 percent hydrochloric acid in the feeder where the acid concentration is reduced to 18 or 20 percent because of the moisture in the wood. The chips and hydrochloric acid solution flow down the slanting tray where prehydrolysis is completed in 45 minutes. Hydrochloric acid solution containing pentose is separated from the wood chips by means of a filter and a portion of the solution is recycled to the mixer at the top of the column. Sugar in the prehydrolysis solution is concentrated to 20 or 25 percent by the recycling operation. Prehydrolyzed material is drained and goes down the column with 30 percent hydrochloric acid at a temperature below 10° C while hydrogen chloride gas is introduced at the bottom. The hydrochloric acid solution flowing down the column absorbs the hydrogen chloride gas and increases in concentration to 41 or 42 percent as the main hydrolysis occurs. The hydrolyzed material coming off the bottom of the column enters a drying chamber where it is dried by dry hydrogen chloride gas which has been washed and dried with concentrated calcium chloride solution. A solid mixture of sugar and lignin is obtained from the right end. The sugar is extracted with water and post hydrolyzed.

After a preliminary study initiated by the Naguchi Institute and the Shin Nippon Chisso Herija Co. a process known as the Naguchi Chisso Process[19,20,21,22] was developed. This process featured the handling of wood particles in their original form throughout and the conducting of the prehydrolysis and main hydrolysis in the interior of the wood particles. In particular the main hydrolysis is carried out with hydrogen chloride gas in a fluidized bed.

Wood flour produced by crushing logs or sawdust is used as a raw material. This material is permeated with 0.5 to 0.7 times the quantity of 3 to 5 percent hydrochloric acid. Prehydrolysis is carried out by introducing steam at 100 to 130° C. The prehydrolyzed wood is extracted by a counter flow current of water to get a sugar concentration of 10 to 15 percent. The prehydrolyzed wood is flash dried by hot air and then permeated with hydrochloric acid solution below 38 percent concentration. The material, permeated with hydrochloric acid and containing sufficient water for the main hydrolysis, absorbs hydrogen chloride gas while being fluidized with cold hydrogen chloride gas. The acid concentration in the acid permeated material reaches 42 percent. Hydrolysis does not take place up to this point.

The material which contains a high concentration of hydrochloric acid by saturated low temperature absorption is rapidly heated to 40 or 45° C to complete the hydrolysis while being fluidized with hot hydrogen chloride gas. Saccharification of wood cellulose proceeds almost immediately.

The material from the main hydrolysis is apparently solid. This is dried in hot hydrogen chloride gas to vaporize the permeated and absorbed hydrogen chloride. Sufficient hydrogen chloride is left in the sugar material to carry out post hydrolysis.

In a second test process, hydrogen chloride absorption at low temperatures and main hydrolysis by raising the temperature are carried out while transporting acid permeated material with hydrogen chloride gas by a pneumatic conveying method. Particles are carried through a deacidification process by means of penumatic transport with high temperature hydrogen chloride gases. This process is called flash saccharification and if the ripening period of the process is omitted, the entire process of

hydrochloric acid absorption, heating, and hydrochloric acid recovery can be carried out in a few seconds. The yield of sugar by the main hydrolysis is 95 percent and if the sugar decomposed in the acid recovery process is deducted the total yield is 90 percent. These processes have problems similar to those discussed earlier; recovery of hydrochloric acid economically, unavailability of construction material for equipment and the complicated nature of material handling problems.

2. DILUTE ACID HYDROLYSIS

The dilute sulfuric acid processes were developed because economic recovery of acid in concentrated acid processes has not been achieved and yields are low with the use of small amounts of concentrated acids. These processes are reviewed very thoroughly by Wenzel[23].

(1) Scholler Process

In the early Scholler[24] process 0.5 to 1 percent sulfuric acid is introduced continuously under pressure from the top of the saccharification column, and the saccharified solution is continuously discharged from the bottom to remove the sugar from the reaction system as soon as possible to minimize degradation of the sugar. Later the process was modified by introducing the acid intermittently. A final modification was the development of the cold shove process which increases the charge of wood in the reactor by compressing it several times with high pressure steam.

The hydrolysis column in the Scholler process is called a percolator. The wood chips are packed in the percolator and then compressed with steam at about three atmospheres. More chips are added and compressed with steam. This procedure is repeated several times, compressing the charge which increases

the wood chip bulk density by a factor of two. Acid for hydrolysis is introduced under pressure and then expelled by steam. Fresh acid is not introduced immediately after the saccharified solution has drained from the wood chips, but the temperature is maintained by introduction of steam. Hydrolysis proceeds during this period by the acid which has permeated the wood. Acid is rapidly introduced again and the solution containing the sugar is discharged from the percolator. As a result of a pressure difference produced between the wood and the acid, the saccharified solution in the pores of the wood is expelled. The residence time of the sugar is shortened in this process and, therefore, the quantity of sugar decomposed is reduced.

(2) Madison Process

The Madison process developed at the Forest Products Laboratory is a modification of the Scholler Process. In this process 0.5 percent sulfuric acid is fed continuously into the reactor at a fixed rate. The wood feedstock is crushed as small as possible to increase the rate of acid permeation into the interior of the wood.

After prehydrolyzing at 135 to 150° C to remove the hemicellulose, the main hydrolysis is conducted by introducing 0.5 percent sulfuric acid under pressure at the top and continuously removing a solution from the bottom. The reaction temperature during the 3 hour hydrolysis time is raised from 150° C to 190° C. When the sugar concentration reaches about 1 percent near the end of the reaction the saccharified solution is introduced to the next percolator and the sugar concentration maintained at about 5 or 6 percent. Sugar yields as high as 75 percent are expected.

(3) TVA Process

The TVA Process[25,26] is a modification of the Madison process with the objectives of designing simpler equipment and

producing a more concentrated sugar solution. According to Russian investigations[27] the hydrodynamic flow conditions in the vertical percolation process have not been sufficiently utilized. They have combined vertical percolation with horizontal flow, which has the advantage of assuring practically unlimited flow of hydrolyzate. The yield of reducing sugars has been increased by 15 to 20 percent with the increased flow of hydrolyzate.

Some problems were associated with the dilute sulfuric acid hydrolysis processes described above. Since the operating conditions are very severe, high priced construction materials are required, making it a capital intensive operation. The sugar concentration in the acid hydrolyzate is about 5 percent, thus making it essential to include a multistage evaporator in the process stream which adds to the cost of equipment and also increases the process energy required. Most of these processes are semicontinuous which is less desirable in terms of material handling.

3. WEAK ACID HYDROLYSIS

Another process which deserves some attention is the weak acid or auto hydrolysis process described by Snyder[28] in his patent. This process requires that the woody material be initially impregnated with an alkaline or buffer reagent and then subjected to elevated temperatures of 250 to 300° C and pressures of 600 to 1250 psi for a short period of time. The amount of alkali or buffer added is the amount necessary to keep the pH at the end of the reaction between 3.1 and 3.4. The reaction times varies from about 60 seconds to 5 minutes according to the pressure and the amount of alkali.

In this process approximately 30 percent of the pentoses are converted to furfural and with post hydrolysis approximately

80 to 90 percent of xylose and glucose can be recovered. This type hydrolysis is being evaluated by Georgia Tech in a modified form using batch and continuous steam explosion devices and results will be published at an appropriate time.

IV. PROCESSES UNDER DEVELOPMENT

Several new processes are currently under development and may have commercial potential. The more important of these are described in this section.

1. GRETHLEIN PROCESS

Dr. Hans Grethlein[29,30] at Darthmouth has proposed a continuous process for hydrolysis of wood using dilute sulfuric acid. He based his design on an analysis of the reaction kinetics to optimize the conversion to glucose and minimize the degradation of products. The resultant reactor was determined to be plug flow isothermal with a residence time of 0.19 minutes at 230^{o} C using an acid concentration of 1 percent.

The specific design proposed is based on newsprint as a feed material. In this design the newsprint is prepared by a pulper which is used to repulp waste newsprint. The resulting slurry is pumped through a liquid cyclone to remove minor particulate foreign matter. Dewatering screws remove enough water to give a 13 percent slurry. This slurry is pumped to a preheater and then to the reactor. Sulfuric acid at 50 percent concentration is added and final heating is carried out with live steam. The live steam addition reduces the slurry concentration to a nominal 10 percent. The reaction time is stopped by a flash tank. The flashed liquid acid hydrolyzate is pumped to a neutralizing tank where the acid is neutralized with lime. The unreacted lignin, cellulose, and calcium sulfate are removed by a continuous centrifuge.

The advantage of this process is that equipment size can be greatly reduced since the reaction time is on the order of

seconds instead of hours as with the previously described batch systems. The disadvantages associated with this process are that maximum solid content of the slurry must be between 12 to 15 percent; the maximum conversion reported is up to 55 percent; and severe operating conditions necessitate the use of expensive alloy for the hydrolyzer, pump, and equipment associated with this stage thus making it capital intensive.

2. PURDUE PROCESS

George Isao at Purdue University has developed a unique process for hydrolysis of wood using dilute sulfuric acid or enzymatic hydrolysis[7,31]. The Purdue process consists of three main operations; first a dilute acid pretreatment, second, a solvation to modify the cellulose structure and last, a hydrolysis and separation of the hexose sugar.

The feed material is first ground or chipped and then prehydrolyzed with dilute sulfuric acid. The prehydrolyzate is separated, neutralized and discharged for further processing. The residue is dried to 10 percent moisture in a low pH condition and then intimately mixed with concentrated sulfuric acid which dissolves the cellulose. The cellulose is then precipitated by the addition of methanol. The precipitated cellulose is amorphous and is easily hydrolyzed by acid or enzymes to glucose. This process can be classified as a pretreatment method. Some of the drawbacks associated with this process are the recovery of methanol and acid. Unless the recovery systems are perfected this process will remain uneconomical.

3. TAMPELLA-POHJOLA PROCESS

Pohjola[32] has conducted sequential multibatch dilute acid hydrolysis using 0.2 percent H_2SO_4 and 475° F with blow-down of straw. A 44 percent increase of the rate constant for cellulose hydrolysis was observed from the first batch to the second batch. This was attributed to the blow-down. The rate

constant did not change for subsequent batches. An overall sugar yield of 70 percent was obtained. A material balance for this process is shown in Exhibit IV-1.

Pohjola used the above information for the conceptual design of the Tampella-Pohjola process. The process consists of one or two stages. In the two-stage process the first stage serves as the prehydrolysis step for removing the easily hydrolyzable carbohydrates. A two-stage process is desirable when high yields of both pentoses and hexosos are preferred because then the process conditions can be chosen independently for each step.

In the main hydrolysis fresh feed that has been prehydrolyzed and blown in the case of the two-stage process is mixed with the recycled solid and charged continuously into a continuous Tampella digester by plug screws. Steam and hot dilute sulfuric acid are injected into the reactor immediately after the feed point. The reaction mixture in a low liquid to solid ratio is mixed and transported along the reactor tube by a screw conveyer until discharged continuously into an atmospheric blow cyclone. The blown material is diluted in the cyclone with hot water or hot recycled sugar solutions and pumped into the first separator. Here the hydrolyzate, together with the finest solid fraction, is removed from the rest of the solid which is returned to the feed screw.

The hydrolyzate is clarified in the second separator. The lignin fraction may be washed free from residual sugars and acid in an additional stage.

The process is characterized by a great flexibility with respect to raw material quality and to the selection of process parameters such as reaction temperature, acid concentration, reaction time and recycle ratio. The yield of sugar and its concentration in the hydrolyzates can be adjusted within fairly wide ranges.

EXHIBIT: IV-1
TAMPELLA-POHJOLA PROCESS

RAW MATERIAL	Kg/100 kg dry straw
Straw	
- Cellulose	35.9
- Hemicelluloses	34.7
- Lignin + Ash	20.7
- Other	8.7
PRODUCTS	
Prehydrolyzate	
- Pentoses	18.0
- Hexoses	3.0
- Other	14.0
Main Hydrolyzate	
- Hexoses	28.0
- Pentoses	2.0
- Other	6.0
Lignin	28.0
CONSUMPTION	
Steam	
- Prehydrolysis	45.0
- Main Hydrolysis	90.0
Sulfuric Acid	
- Prehydrolysis	1.5
- Main Hydrolysis	1.5

A pilot plant for the Tampella-Pohjola process is under construction in Sweden. The process represents a variation of continuous dilute acid hydrolysis, but the Tampella digester does not operate at temperatures above 210° C. High temperature, high solids, and low residence times are required for good yields. Substantial modifications of the Tampella digester must be made before it can be used commercially as a dilute acid cellulose hydrolysis reactor.

4. WAYMAN PROCESS

In the Wayman process[33], wood chips are first subjected to steam explosion autohydrolysis. Lignin is then extracted from the steam exploded wood using a caustic solution. The delignified wood is then hydrolyzed with dilute acid in sequential multiple batches. This later step consists of multistage hydrolysis that essentially represents a plug flow reactor with cellulose recycle.

The autohydrolysis of wood at a 50 percent moisture content was carried out with 195° C steam and a 30 minute retention time. This step was conducted in a batch type operation using a 30 ml. pressure vessel and also in a continuous mode using Stake Technology system at 250 psi. This step results in the formation of volatiles such as furfural, water soluble hemicellulose and alkali soluble lignin. Typically about 12 percent of the wood is converted to volatiles, 12 percent of hemicellulose is obtained in the water washings of residue, and 75 percent of the wood remains readily disintegrated fibrous pulp. After water washing, the autohydrolyzed pulp is extracted with a 2 percent sodium hydroxide solution held at 70° C for 2 hours to remove lignin. The cellulosic residue has 97 percent cellulose as compared with 50 percent in the starting wood.

The acid hydrolysis is carried out in a 30 ml pressure vessel at 190° C with 0.5 to 4 percent dilute sulfuric acid. In a single

stage batch system using dilute H_2SO_4, the maximum saccharification is 42 percent of the theoretical value. In a multi-stage hydrolysis with 2 percent H_2SO_4, at 190° C and 20 minutes retention time the overall conversion of cellulose to sugars is up to 80 percent. The remaining steps utilize conventional technology for the fermentation and distillation stages.

5. NEW YORK UNIVERSITY PROCESS

The New York University process[34] involves continuous dilute acid hydrolysis using an extruder. A Werner and Pfleiderer (53 mm) ZDSK53 twin screw extruder is used for conveying, mixing and extruding the required amounts of lignocellulosic biomass at predetermined temperature, pressure and throughput rate.

The feed for the extruder must be relatively fine particles such as saw dust or pulp in a slurry. The biomass is dewatered to 40 to 60 percent solids using a dewatering screw and then is fed to the extruder. Sulfuric acid is injected into the biomass followed by steam injection. Yields of 50 to 60 percent have been demonstrated in the reactor. An economic analysis of the process gave an ethanol production cost of $1.08/gal. The cost of the extruder is based on SS316 as the wetted materials of construction. Rugg hypothesizes that the lignin component coats and protects wetted metal parts of the extruder. This is based on his visual observations after a short operational life. The extruder in any case is a very capital intensive reactor as compared to other plug flow reactor systems. Lignin remains with the hydrolyzate and the resulting mixture is a plastic like mud.. Separating the lignin from the sugar appears to be a formidable task.

6. GERMAN PROCESS

A german team has developed and patented a process[35] which has excellent potential for producing fermentable sugars from

lignocellulosic biomass. They have developed a process for the production of glucose from cellulose containing vegetable raw materials which can be disintegrated by steam pressure treatment. The feed materials are treated with saturated steam at temperatures of from 160° C to 230° C for a period of 2 minutes to 4 hours. The raw material that has been steam exploded or disintegrated this way can be extracted with an aqueous solution of alkali to remove lignin. The residual cellulose can then be subjected to acid or enzymatic hydrolysis.

This patent appears to cover most of the operating conditions and looks like a step in the right direction. A Georgia Tech team is presently evaluating this patent.

7. AUBURN PROCESS

Professor Chambers[36] and his team have been developing a process of selective acid hydrolysis of hemicellulose to xylose and then to ethanolbutanediol column fermentation. From the study of acid hydrolysis it was determined that a maximum xylose yield of 83 percent is obtained from the hydrolysis of hemicellulose in oak wood at 150° C, 0.2 percent H_2SO_4 and 90 minutes residence time. At these conditions, the soluble xylans account for about 9 percent of the original xylan content of the oak biomass. The conversion of hemicellulose to furfural is about 8 percent. This kinetic study was conducted using a fixed bed type reactor.

The fermentation stage involves the use of a column packed with porous ceramic rasching rings with microbes attached. By means of a recirculated batch operation of the column fermenter, a 10 percent xylose solution is fermented within 50 hours to produce 3.4 percent butanediol and 1.2 percent ethanol. Attempts are being made to convert it to a continuous process. This process is still in a bench scale stage.

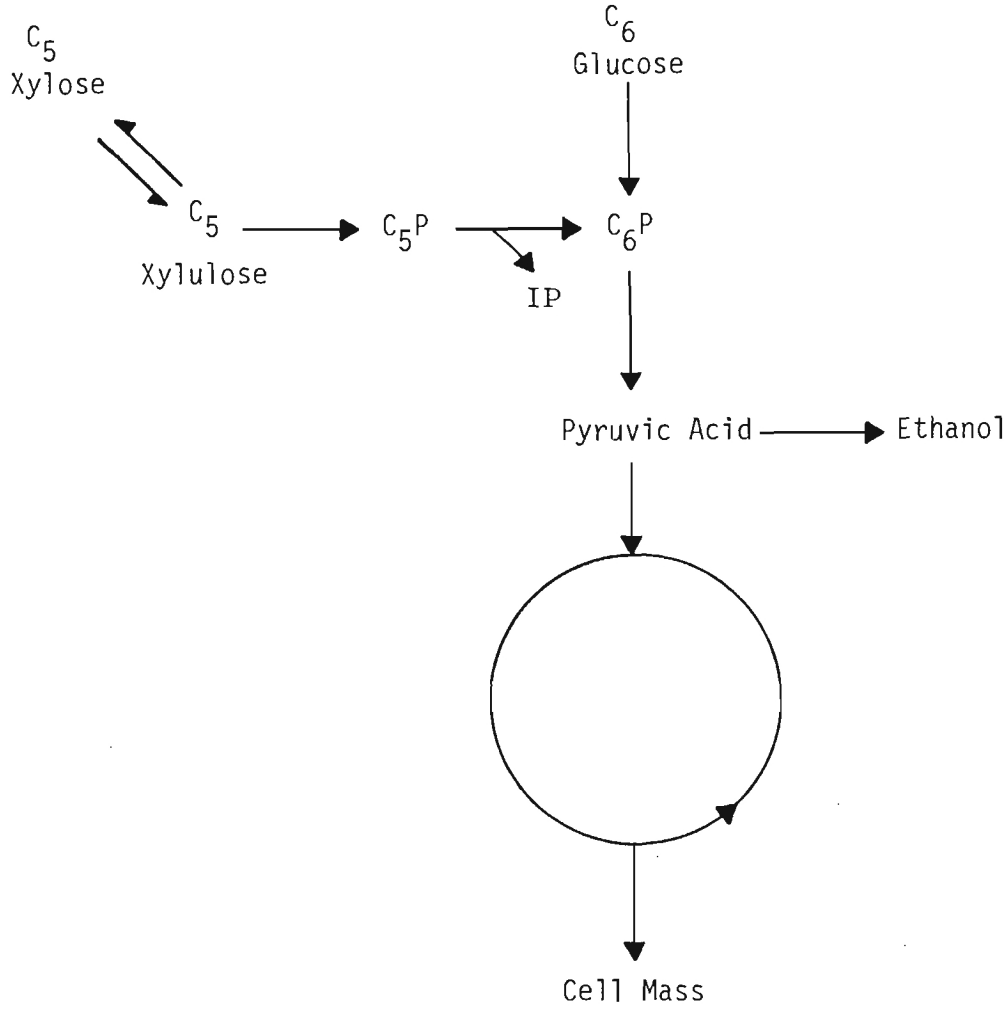
8. PURDUE PROCESS-XYLOSE TO ETHANOL

Tsao and Flickinger[37] of Purdue University have discovered that converting xylose into xylulose by xylose isomerase enzyme makes xylose readily fermentable by an ordinary saccharomyoes yeast. A 10 percent xylose solution can be produced by dilute acid hydrolysis of bagasshemicellulose. The isomerization reaction and production of ethanol is given in Exhibit IV-2. The major current problems include the equilibrium conversions and neutral pH requirement for enzymes which are not favorable for the fermentation stage.

9. GEORGIA TECH PROCESS

The Georgia Tech process is being developed at bench and pilot scale. It will not be discussed in this report.

EXHIBIT IV-2
GLUCOSE AND XYLOSE



V. SUMMARY

Conversion of cellulosic biomass to fermentable sugars can be economically viable if:

- The pretreatment method is cost effective
- Hydrolysis of cellulose to glucose is maximized at an optimum cost
- Byproducts are recovered
- Process is continuous and does not consume too much energy
- Capital required to build the plant is competitive.

Among all the pretreatment processes discussed, the steam explosion method appears to be the most desirable. The Stake reactor operated continuously under less severe conditions of temperature and pressure is far superior to the batch Iotech system.

In the hydrolysis step the use of concentrated acid is most attractive. Since no cost effective method to recovering acid has been developed, the use of concentrated acid in the hydrolysis step is unfortunately not feasible.

Historically, dilute acid for the hydrolysis of biomass has been used extensively. In the Scholler process batch addition of dilute acid for the hydrolysis of wood is responsible for the long residence time of 16 to 20 hours, the low concentration of reducing sugars, and the excessive consumption of chemicals. The steaming and the rest periods between the

batches of acid promote the decomposition of sugar and contribute to the short life of the valves and other equipment. The Madison process is a modified and improved Scholler process. In this process a method of automatically controlled continuous addition of the acid and controlled removal of the sugar solution from the bottom to avoid its decomposition are developed. In the Madison process the weight ratio of wood to acid is 1:3 as compared with 1:10 in the Scholler process. The reaction time in the Madison process is 2.8 hours as compared with 15 to 18 hours in the Scholler process. The above two processes are batch in terms of solid handling.

Considerable improvements have been made by introducing a continuous flow reactor in the Grethlein process. This approach has simplified the material handling problems. More recently the concept of continuous flow reactor has been modified further by introducing extruders in the New York University process. The advantage of this system is that a feed slurry with a very high solid concentration of up to 40 percent can be fed to the reactor thus producing a much higher sugar concentration in the exit stream. The disadvantages of using this improved system are that extruders for this type of operation can be energy intensive, and capital intensive. Some of the products such as pentoses can be lost during the operation.

Finally the most improved hydrolysis method under investigation is proposed by a GIT team. In this design a Stake Technology reactor is used. A feed slurry of pure cellulose with up to 35 percent solids is fed in this continuous flow reactor with a recycle of unhydrolyzed solids. This can give conversion of cellulose to sugar up to 80 percent.

The Wayman process in many ways resembles the Georgia Tech process. The sequential multi-batch hydrolysis employed by Wayman is equivalent to a recycle plug flow reactor as being

investigated by the Georgia Tech team. A recycle plug flow reactor is less capital intensive than a multi-batch reactor system. The recovery of byproducts such as pentoses, furfural and lignin as proposed in the Georgia Tech process make it economically viable. Some of the important acid hydrolysis processes are compared in Exhibit V-1.

EXHIBIT V-1

ACID HYDROLYSIS PROCESSES

Process	Reactor	Operation Mode	Acid	Acid Concentration			Temperature			Raw Material	Conversion	Sugar Conc in Hydrolyzate	Yield of 95% Ethanol Gallons	Comments
				Pre Hydrolysis	Main Hydrolysis	Post Hydrolysis	Pre	Main	Post					
Bergis Rheinau	Series of Counter Current Diffusers	Continuous	Fuming Hcl		41%			30°C		Soft wood (coniferous)		30%	83.4	1. Main problem was the economic recovery of acid
Hokkaido		Batch	Conc. H_2SO_4	1-2%	80%	2%	140-150°C	Room	100°C	Hardwood	85%	-	-	1. Glucose was produced. 2. Uneconomic recovery of acid.
Scholler	Packed Bed	Batch	Dilute H_2SO_4	0.6%	0.6%	-	134°C	170°C 8 atm	-	Softwood (coniferous)	-	4%	60	1. Acid stationary. 2. Reaction period 15-18 hrs.
Madison	Packed Bed Percolation	Semi-Continuous	Dilute H_2SO_4	0.5%	0.5%	-	150°C	185°C 9 atm	-	Softwood (douglas fir)	-	5%	64.5	1. Acid flow-continuous. 2. Reaction time 2-8 hrs
Russian Process	Packed Bed with vertical percolation and horizontal flow of dilute H_2SO_4	Semi-Continuous						Not known						Improved hydrodynamic flow increases acid throughput rate leading to 15-20% increase in the yield of reducing sugars.
Grethlein	Plug flow	Continuous	Dilute H_2SO_4	-	1%	-	-	230°C	-	Waste Paper	55.3%	-	56.5	1. This at pre-pilot scale 2. Ethanol figures are projected from glucose yield.

EXHIBIT V-1 (Continued)

ACID HYDROLYSIS PROCESSES

Process	Reactor	Operation Mode	Acid	Acid Concentration			Temperature			Raw Material	Conversion	Sugar Conc. in Hydrolyzate	Yield of 95% Ethanol Gallons	Comments
				Pre Hydrolysis	Main Hydrolysis	Post Hydrolysis	Pre	Main	Post					
Purdue	Not specified	Semi-Continuous	Dilute H_2SO_4	1.9%	0.5%	-	121° C	125°C	-	Corn Stover	-	-	46.6	1. Economic recovery of concentrated H_2SO_4 from pretreatment stage is a problem 2. Degradation of Methanol adds to the cost
Tampalla PohJolla	Pressure Vessel	Batch	Dilute H_2SO_4	-	0.2%	-	-	200°C	-	Straw	70%	-	45.6	Bench scale operation
Wayman	Pressure Vessel	Batch	Dilute H_2SO_4	-	0.2%	-	-	190°C	-	Aspen Wood	80%	-	58.4	1. Bench scale operation 2. Series of batch units
Georgia Tech	Plug flow with recycle	Continuous	Dilute H_2SO_4	-	1%	-	-	210°C	-	Hardwood	77.5%	13%	59.8	One ton per hr Stake reactor is used.
NYU Barry Rugg	53 mm Twin screw extruder	Continuous	Dilute H_2SO_4	-	1-2%	-	-	230°C	-	Sawdust Hard and Softwood Waste Paper	60% Based on available alpha cellulose	8-10% for Hardwood	47.3	1. This process being capital intensive and energy intensive needs more R&D work before becoming commercially viable.

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